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Switchable adhesives for carpet tiles: a major breakthrough in sustainable flooring

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The estimated sales for carpet tiles in the EEA is 45 million m^2 representing both an enormous resource and environmental burden with *ca.* 70 million kg of tile incinerated or landfilled every year in Europe alone. To alleviate the end-of-life problem a facile route to disassemble the multi-layered tiles is needed, but this is currently impractical due to the powerful adhesives used to bind the layers. Herein we report on a novel starch based adhesive, which is not only effective at binding the layers but is switchable, using an inexpensive treatment, derivable from a renewable and low cost resource and provides a remarkable degree of flame retardancy to the carpet tile. Our results not only show how we can reduce a massive product-specific waste problem, but also demonstrate a more general approach to greener product design encompassing end-of-life considerations.

Introduction

The estimated sales for carpet tiles in the EEA is 45 million m^2 or over 100 million kg per annum. This represents both an enormous (largely non-renewable) resource (*e.g.* 50 million kg of bitumen) and environmental burden with *ca.* 70 million kg of tile incinerated or landfilled every year in Europe alone.[1] To alleviate the end-of-life problem we need a facile route to disassemble the typically multi-layered tiles, but this is currently impractical due to the powerful adhesives used to bind the layers.[2] The challenge for researchers and for industry is to design a carpet tile that is both durable for intensive use over a number of years, but is also easily disassembled into useful components when no longer required for its original purpose.[3] Herein we report on a novel adhesive which is not only effective and switchable (reverts from binding the fabric and backing layers to not, enabling their separation) using an inexpensive treatment, but is also derivable from a renewable and low cost resource and provides a remarkable degree of flame retardancy to the carpet tile. The adhesive can be derived from a number of common types of starch. Our results not only show how we can reduce a massive product-specific waste problem, but also demonstrate a more general approach to greener product design encompassing end-of-life considerations.

Disposal of post-consumer carpet tiles and waste from manufacture such as off-cuts produces large volumes of non-readily degradable waste for landfill, such as bitumen, PVC, SBR-latex and nylon. This has been exacerbated over the last 20 years with the demand for carpet tiles dramatically increasing. Carpet tiles can be more resource efficient than full floor carpets since individual tiles can be replaced when worn or damaged. Of the large volume of sales in the EEA, largely in the B2B market, some 50 million kg of bitumen and 10 million kg of Nylon are consumed. The waste bitumen can be relatively easily chopped and melted back into the backing layer of the tile. Nylon however cannot be recycled with adhesive contamination present without downgrading the material. This means virgin nylon has to be used in the fabric layer of all new tiles produced.

The electrical energy required to produce Nylon is 3.43 kWh kg^{-1} Nylon,[4] and for every kWh of electricity, 0.1661 kg CO_2 (primary source) is produced.[5] By using a switchable adhesive it should be possible to recycle the nylon face fabric in new carpet tiles. This considerably reduces the 5697 tonnes of CO_2 emitted into the atmosphere during production of the virgin nylon needed to make current volumes of tiles. Additionally, the Global Warming Potential (GWP) of the Nitrous oxide produced while forming the required amount of adipic acid used to manufacture the same amount of Nylon 6,6 is $4.5–5.2 \times 10^8$ kg CO_2 equivalents.[6-8] The greater part of this may be saved by recycling the nylon. It can therefore be seen that post-consumer disposal is a serious environmental concern with pressures to rectify these issues coming from manufacturers, governments and from the general public.[9]

The current manufacturing process for carpet tiles involves the use of powerful adhesives such as styrene-butadiene-rubber (SBR) latex to anchor the pile fibres, which are usually nylon 6,6 to a polyester fabric and a backing of bitumen.[10] The adhesion is such that disassembly of the carpet tile is effectively impractical and the tile components cannot be recycled.[3] At present the bulk of waste carpet tiles are landfilled or incinerated with over 65 million kg of material having that fate each year in Europe alone. This represents an enormous and increasingly unacceptable burden on the environment especially as landfill sites fill up. We are also destroying enormous quantities of materials constructed from non-renewable resources that are becoming more scarce.

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We need to make environmental improvements at both the raw material and end-of-life stages in the life-cycle of tiles. In particular we need to adopt the benign-by-design approach advocated by green chemistry.[11] Herein we describe an approach based on the replacement of traditional, non-sustainable and fossil-derived irreversible adhesives with a novel, switchable and renewable adhesive based on starch.

Starch adhesives have been used for thousands of years and are still used to bind various paper and cardboard products including stationery, wallpaper and packaging. They have also been shown recently to have potential application for bonding metal.[12] However, in general their more widespread use has been hampered by instability towards water and poorer mechanical properties compared to both cellulose and synthetic derived polymers.[13]

There are various options for diverting used carpet tiles from landfill or incineration, such as, rejuvenating the tile with sophisticated cleaning techniques.[14-15] This can extend the life of the tile but, it is inevitable that the tile will eventually need disposal. Chopping and downgrading tiles into roofing materials *etc.* or into more backing layer, reducing disposal and mining of mineral fillers is another option that has been tested in the past but this is still far from satisfactory as more valuable nylon is needed for the fabric layer.[16] Of all the options to achieve full recyclability of the tiles, the most preferable is to mechanically separate the main layers by pulling apart the fabric and backing layers.[17] This has been tried but again the powerful adhesives currently used to bind the layers hinders this method, as the layers must separate cleanly without leaving adhesive on the nylon fibres. Reducing the contamination in the separate layers is the biggest obstacle to an increased use of recycled fibre.[17] However, by applying a switchable starch adhesive we can not only separate the layers with the application of a simple and cost-effective stimulus but also easily remove the adhesive from the layers (so that the starch can also be recovered). (see Fig. 1).

Materials and methods

Materials

All reagents and materials were obtained from Aldrich and used without further purification. Solvents were obtained from Fisher Scientific. The carpet tile upper fabric layer and the bitumen backing layer were obtained from InterfaceFLOR's production line.

Expanded starch preparation

Starch (200 g, 1.23 mol) was added to 4 dm^3 of distilled water in an adapted All American pressure canner 915 (~14.7 dm^3) to enable the components to be stirred. The mixture was then agitated at 110 °C for 3 h to gelatinise the starch, forming a clear gel. The gelatinised starch was then cooled to room temperature and placed in a fridge at 5 °C for 3 weeks (an excess time period was chosen to ensure complete crystallisation. In practice, less than one day is needed) within hermetically sealed containers (4×1 dm^3). After, the water within the aquagel was exchanged by mixing it for 15 min with 1.5 dm^3 of ethanol to precipitate it out using an overhead stirrer, leaving it to settle, and then

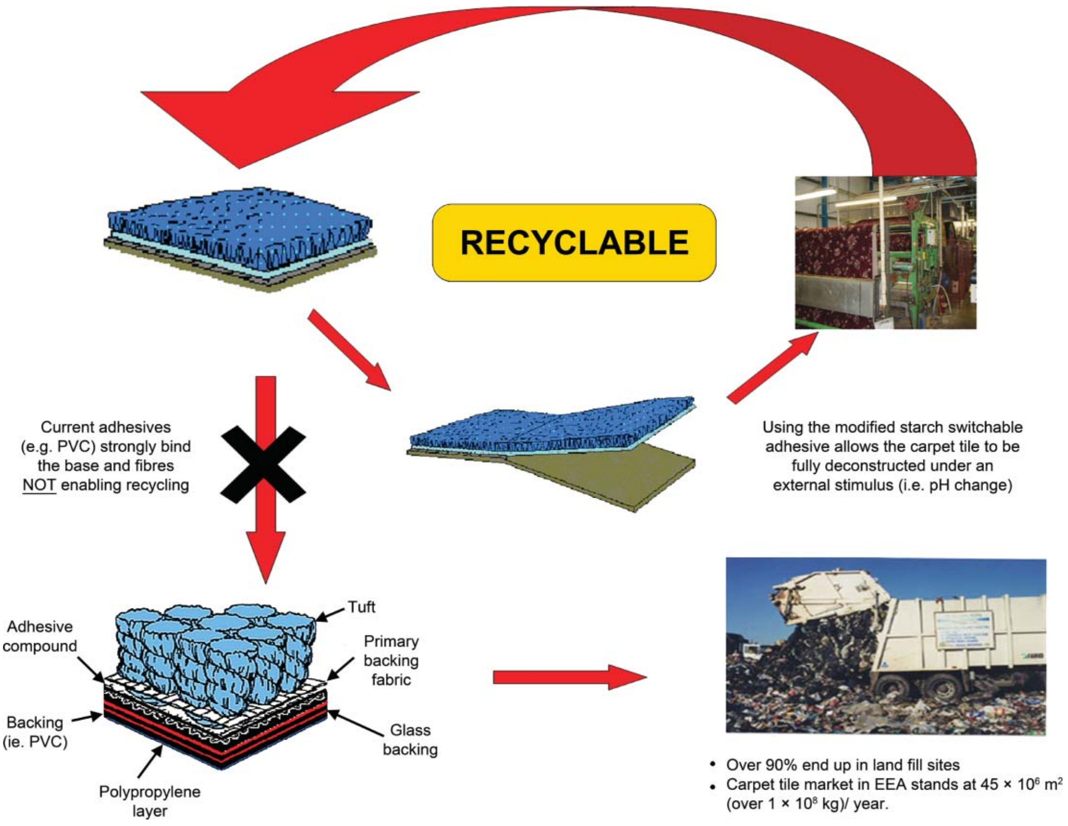

Fig. 1 Schematic highlighting the goal of full recyclability through use of a modified starch 'switchable' adhesive.

filtering. This process was repeated a further two times (2 × 1.25 dm^3 ethanol) before placing the material in a vacuum oven (< 150 Pa) set at 50 °C for 12 h. A fine white powdered, expanded starch was yielded (192 g, 96%) with a surface area of 163 m^2 g^{-1}.

Acetylation

Expanded starch, 192 g (1.19 mol) was added to a 2 dm^3 flanged flask and to this 1.2 dm^3 of toluene was added followed by 370.5 g (3.63 mol) acetic anhydride. The mixture was heated to 90 °C and stirred for 5 min; after which 2 g (16.4 mmol) 4-(dimethylamino)pyridine (DMAP) was added. The reaction was maintained at 90 °C while stirring for 12 h. The mixture was then cooled to 50 °C and 350 cm^3 ethanol added. The precipitate formed was stirred for ten minutes, filtered, and washed with a further 350 cm^3 of ethanol before drying the product (332 g) for 24 h at 20 °C under reduced pressure. Acetylation was confirmed by DRIFTS, checking the ester peak at 1749 ± 4 cm^{-1} and also by titration (D.S. = 2.6). Further conformation of acetylation was that the decomposition dTG peak using STA had changed from 305 °C to between 370 and 380 °C. Nitrogen adsorption porosimetry was used to determine the surface area (107 m^2 g^{-1}) of the acetylated compound.

Material characterisation

Nitrogen adsorption/desorption measurements were carried out using a Coulter™ SA3100 Surface Analyser™ at 77 K on expanded starch and the acetylated expanded starch (~ 0.1 g). Prior to analysis, the sample was out-gassed for 3 h at 65 °C and mass differences corrected after the experiment. The resultant data was analysed for BET surface area using Coulter™ SA View™ software 1.01.

The titration method employed to determine the degree of substitution (D.S.) of the acetylated starch was based on the procedure employed by Wurzburg.[18] Accurately weighed acetylated starch (1.0 g) that had been finely ground was placed in a 250 cm^3 flask, and 50 cm^3 of 75% ethanol in distilled water added. The loosely stoppered flask containing the slurry was agitated at 50 °C for 30 min. It was then cooled to room temperature, and 40 cm^3 of 0.5 mol dm^{-3} KOH added. The mixture was left for 72 h with occasional stirring. Excess alkali was back-titrated with 0.5 mol dm^{-3} HCl using phenolphthalein as an indicator, after which it was left for a further 2 h, and any additional alkali which may have leached from the solid sample titrated. A blank using the original unmodified starch that was used as the base for modification was tested, and also duplicate samples were tested in a similar manner.

Spectra were recorded at room temperature on a Bruker Eqinox 55 FT-IR spectrometer using a fast mercury–cadmium telluride (MCT) detector. Expanded starch or acetylated expanded starch samples were accurately weighed out together with potassium bromide in a 1 : 9 ratio respectively. The two components were mixed thoroughly to ensure homogeneity. Samples were then tested using the DRIFTS program using the Bruker Optik GmbH (1997–2005), Opus version 5.5 FTIR software.

STA analysis of hydrolysed starch was carried out on a Seiko™ instruments Incorporated SII Exstar 6000™, TG/DTA 6300™ using approximately 15 mg of material accurately weighed in to a platinum sample pan. An empty platinum pan was used as reference. The sample was then heated in a nitrogen flow from 20 °C to 625 °C at 10 °C min^{-1}. Analysis of the dTG value was carried out using the Seiko™ instruments Incorporated SII Exstar 6000™, TG/DTA 6300™ dedicated analysis software.

Switchable adhesive preparation

The acetylated expanded starch (332 g) was added to acetone (3 dm^3) and glyceryl triacetate (GTA), 111 g (0.508 mol) in a standard paint tin and homogenised until a smooth and consistent paste was formed. The average viscosity using a Brookfield RV Viscometer, spindle number 6, was 23.5 ± 4.5 N s m^{-2} (2.5 rpm) at 25 °C.

Lab scale adhesive application

Two pieces of primary fabric each measuring 10 × 10 cm were weighed accurately for future reference. These were then adhered together using the switchable adhesive (2.7 cm^3, 0.6 g adhesive content) at the ends forming a 2 cm overlap. A 10 × 10 cm piece of non-stick plastic sheeting was then laid on top followed by a 10 × 10 cm metal plate weighing 500 g. This setup was then placed in an oven at 50 °C for an excess amount of time (2 days) to remove water or solvent and to set the adhesive. After this time the plastic film and metal plate were removed and the primary fabric cut into 5 strips, each 2 cm wide. As the adhesive can flow out of the edges and produce a non-uniform distribution there will be discrepancies with the results obtained. Therefore, the adhesive is usually applied to a large sheet, which is then cut in to the desired test samples.[19]

Lab scale adhesive testing

The adhered primary fabric strip was inserted into a tall 500 cm^3 beaker containing 450 cm^3 of the test liquid. These were either distilled water or 0.5 mol dm^{-3} sodium hydroxide solution set at 20 °C, 50 °C and 80 °C. Samples were immersed in the test liquid for 2 min, after they were dabbed dry and tested immediately. Steam was also used to ‘switch’ the adhesive. In this case the bonded fabric was placed on top of the beaker while sufficient energy was applied to maintain a flow of steam from the beaker for 2 min. The control used the original bonded material without further treatment.

Testing was carried out by clamping one end of the primary fabric in to the lower jaw of the Instron Testometric MICRO 350, while the other end was clamped into the upper jaw. Average breaking load (MPa) was obtained from the area of bond contact (2 × 2 cm) and the maximum value obtained from the stress–strain curve conducted at 20 °C, 60° relative humidity with a cross head speed of 1.67 × 10^{-3} ms^{-1} (100 mm min^{-1}). Samples were tested in at least duplicate.

Prototype adhesive application

Pre-weighed, 4 × 500 cm^2 pieces of woven fabric (upper fabric layer of carpet tile) were laid face down and 337 cm^3 (75 g solid adhesive) of switchable adhesive applied per piece of fabric. The adhered fabric was then passed through a doctor blade to ensure the adhesive was applied evenly with a consistent pressure. This was then placed in a ventilated oven at 80 °C for 10–15 min. The sample was then removed and a bitumen backing layer applied, and left to cool.

Prototype carpet tile testing

Industry standard testing was performed on the prototype carpet tiles in accordance to accredited testing procedures, such as the Martindale test depicted in Fig. 2, which assesses wear performance. Fig. 2, also depicts the 'switchable' adhesive paste, and the adhesive after binding the layers of the carpet tile. The switchability test which is currently not a standard carpet tile test was carried out in accordance with BS 7399 guidelines and the flammability testing was carried out by an accredited testing facility.

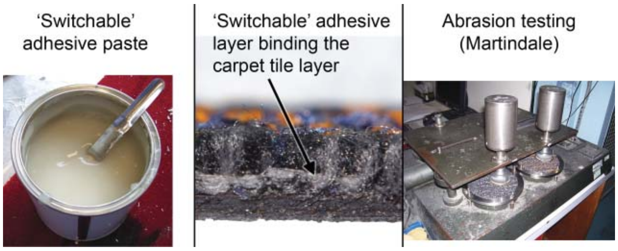

Fig. 2 Schematic depicting the homogenised 'switchable' adhesive, after use, and it upholding under stringent industrial wear testing (Martindale).

Results and discussion

Adhesive preparation

The key properties we need in the switchable starch adhesive to make it suitable for binding the fabric layer to the bitumen backing layer of the carpet tile are:

- A degree of hydrophobicity to allow use under a range of conditions including staining and washing.
- Suitable viscosity and wetting characteristics to enable good penetration of the adhesive into the fibres.
- Ability to undergo plasticization appropriate for application using green and sustainable additives.
- Adhesivity and switchability using an appropriate stimulus.

Corn starch was gelatinised in hot water within a modified pressure canner and then retrograded at 5 °C as described previously. The water contained within the matrix of the retrograded starch was exchanged for ethanol, preventing the collapse of the developed pore structure when dried within a vacuum oven. The surface area and pore volume of the material were tested on a porosimeter (163 $m^2\ g^{-1}$, 0.3 $cm^3\ g^{-1}$). This physical processes of gelatinisation in water and retrogradation of the resulting gel is used to create a metastable form of starch which has an unusually high surface area (*ca.* $>150\ m^2\ g^{-1}$) compared to native starches ($< 5\ m^2\ g^{-1}$) and (*meso*) porosity.[20-21] These metastable materials are stable if protected from the atmosphere but rapidly collapse to low surface area solids when exposed to hot water. We recently described the utilisation of such porous, high surface area starches in the separation of organic compounds in non-aqueous solutions while in a recent US patent their use in odour control was highlighted.[22-23] Apart from applications based on adsorbency we can also take advantage of high surface area to facilitate high degrees of chemical modification and thus control a number of material properties including hydrophobicity and wettability. Modification of conventional starch is possible but, requires much harsher conditions, usually with greater than stoichiometric quantities of reagents. The resulting materials do not have good porosity, hindering formulation. Acetylation was selected as it is relatively cheap, more reactive and retains more of the mechanical characteristics of the native starch compared to starch that has been derivatised with longer (fatty) groups. Acetylation was therefore carried out by transferring the recently expanded material to a toluene solution of acetic anhydride containing a small amount of DMAP as a catalyst. The mixture was heated to 90 °C for 12 h. In this way we were able to obtain a starch with a high degree of substitution of >2.5 (acetylation of hydroxyl groups per glucose unit). This new hydrophobic starch material with good porosity, helping with mixing and hence plasticisation is highly soluble in acetone for example, and readily blends with glycerol triacetate (among similar molecules) to give a plasticised material. The degree of substitution of the acetylated expanded starch was found to be 2.6 as determined from the titrimetric method described earlier. This was also confirmed by checking the ester peak at 1749 cm^{-1} and the absence of a carbonyl peak at 1650 cm^{-1} that would suggest free acetic acid and, hence, indicate a D.S. higher than in practice. The thermal properties of the material were investigated by thermogravimetric analysis (TGA). It was found that the thermal stability of the material after modification increased from 305 °C to 376 °C, making the material more suitable for adhering a wider range of textile materials.

Lab scale switchability trials

Apart from designing a suitable sustainable adhesive to be used within carpet tiles the adhesive needed to be 'switchable' in order that full recycling could be achieved. This was tested as described in the methodology section. The liquids used to 'switch' the adhesive were sodium hydroxide solution (0.5 mol dm^{-3}) and water at different temperatures. Steam was also tested for the same period, but applied in a different manner. The effect that the 'switching' agent has on the breaking load of the adhesively bonded primary fabric compared to the control, can be seen in Fig. 3. The results show that temperature is having a minimal effect on degradation of the adhesive bond, as all samples tested in the different solvents at different temperatures show approximately the same 40% reduction in breaking load. The results using distilled water as the 'switching' agent are somewhat different to those that were treated with sodium hydroxide solution. The sample maintained at 20 °C appears to show a greater reduction in breaking load than the sample at 80 °C. However, within the scope of experimental error it is possible that all samples tested for water show the same 0.1 MPa breaking load, and that the temperature affect on water treatment is negligible. If the median value of the results are correct, it would suggest that the adhesive is being annealed at the higher temperatures, hence increasing the shear stress of the material. It is unlikely that plasticiser leaching is at fault as GTA is only sparingly soluble in water and is very compatible with acetylated starch showing almost ideal plasticiser behaviour

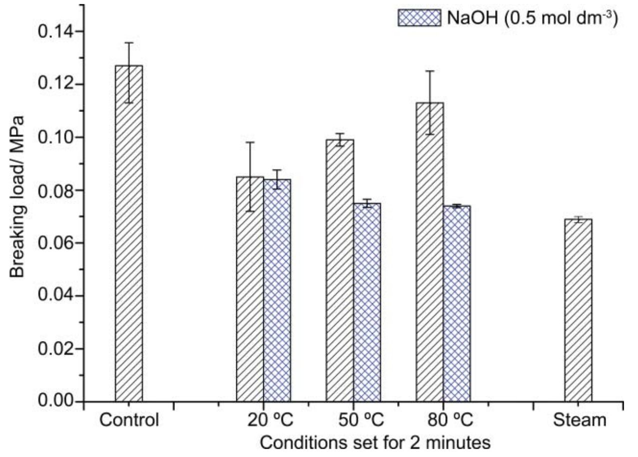

Fig. 3 Graph showing the affect of water and sodium hydroxide solution (0.5 mol dm^{-3}) on breaking load of the adhered primary fabric after testing for 2 min in the conditions described.

with this type of material. Hydrolysis of GTA is also unlikely as it is stable to hydrolysis without the presence of a catalyst.[24–25] From all conditions tested, the result for steam was the best as reduction in breaking load was approximately 50% of the control. This is very promising as using steam brings greater control over the 'switching' mechanism. Instead of soaking the used carpet tiles in a bath, a continuous process could be sought that could be controlled *via* the pressure of the steam, temperature and speed of the process. Overall, the GTA plasticised expanded acetylated starch adhesive shows promising results that were further verified when the adhesive was incorporated into the carpet tile.

Prototype adhesive testing

We produced a 1.35 dm^3 sample of the switchable starch based adhesive that was sufficient to adhere 1 m^2 of carpet tile for carrying out standard industry tests. It was found that our tile passed wear ("Martindale" and "Castor Chair") and impact resistance tests (Hexapod), and the results of the dimensional stability tests (stability to heating at 60 °C for 48 h and submerging in water at 20 °C for 2 h) were excellent. Clearly, the carpet tile held together by the modified starch adhesive has all of the desired properties for construction and use.

The uniqueness of our tile was revealed by the switchability of the adhesion and unexpectedly by outstanding flame resistance results. Whilst the tile had excellent stability to water at room temperature, boiling water caused sufficient reduction in lamination strength (*ca.* 50%) to allow easy separation. The hot water washes off the starch adhesive and does not affect the quality of the nylon or spun bonded polyester fabric thus enabling their reuse. In practice, the pressure with which the face (upper fabric layer) is adhered to the bitumen backing layer is controllable. For these trials the test sample was reheated and additional pressure applied. A little less pressure could further aid 'switchability' by reducing the tendency for the bitumen to flow around the starch coated nylon yarns. Flammability test results were considerably better than almost any commercial floor products; the critical radiant flux (CRF) value obtained of 10.5 kW m^{-2} is only matched by marble floors and similar products. Perhaps not surprisingly in the light of this, treatment with the conventional flame retardant aluminium trihydrate (ATH) had no significant additional effect: the CRF increased by only 0.1 kW m^{-2} and burn length reduced from 130 mm to 110 mm. However, the smoke percentage increased from 49.9% to 67.8% when incorporating ATH into the adhesive. After conducting these flammability tests on the tile with the adhesive incorporated, separate tests were conducted on the adhesive itself using both UL94 flammability guidelines and STA analysis. From these investigations, and those conducted on the prototype tile we believe that this valuable property of flammability resistance is due to the foaming of the starch material at decomposition (*ca.* 370 °C, some 60 °C higher than native starch) creating a carbonaceous intumescent barrier to the heat source. Without this adhesive, the molten nylon would be able to help ignite the bitumen backing layer.

Conclusions

We have proved that expanded starch retains its good surface area characteristics after modification, and is then well suited to adhering carpet tiles that are used in the commercial sectors. The adhesive can also 'switch' under controlled conditions potentially enabling diversion of huge quantities of used tiles that currently end up in landfill. The deconstructed tile backing and fabric layer can now be recycled, achieving a closed-loop system. As an added bonus, the adhesive shows excellent flame retardancy, negating the need for potential hazardous additives and resources. Our discovery can make an enormous contribution to sustainability through waste reduction, increased resource efficiency, and the use of renewable resources. 'spin-off' value of the remarkable flame retardancy of our starch materials may also be dramatic.

Acknowledgements

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